

Volume 17, No. 3 May/June 1995 Sandia National Laboratories

High-temperature reactions of ceramic precursors probed

Ceramic materials, which are corrosion resistant and can withstand higher temperatures than many existing metals and alloys, are of increasing interest for the design of new combustion equipment, such as gas-turbines, steam reformers, heat exchangers, and aircraft and automobile engine parts. A CRF research group, consisting of Mark Allendorf, Tom Osterheld, and Scott Ferko, is using experimental and theoretical approaches developed for

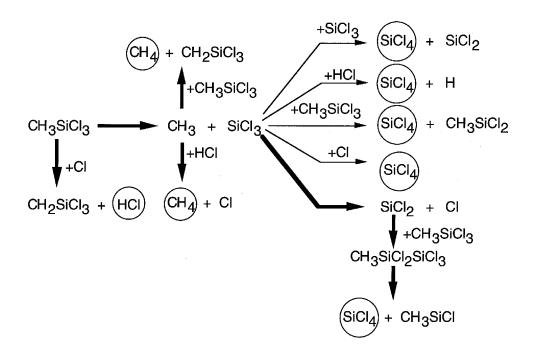
These results will allow MTS decomposition rates to be predicted with greater accuracy...

the study of combustion chemistry to understand gas-phase reactions occurring during formation of ceramics by chemical vapor deposition (CVD). Numerical models derived from these investigations can help industry optimize and scale up new processes for manufacturing composites and coatings. They can also be used to design and test algorithms that use sensors to provide on-line process control.

In recent work sponsored by the DOE Office of Industrial Technologies (OIT), the decomposition of a common silicon carbide (SiC) precursor was examined. Gas-phase decomposition of methyltrichlorosilane (CH₃SiCl₃; MTS) is known to occur under CVD conditions. Unfortunately, the chemistry of chlorinated organosilanes like MTS is poorly characterized, making it difficult to predict decomposition rates and product formation.

Experiments in a high-temperature flow reactor, coupled with ab initio calculations and transition-state theory, yielded the first detailed picture of the elementary reactions occurring during SiC CVD. The results show that MTS decomposition in inert carrier gases such as helium is rate-limited by the unimolecular decomposition of MTS to form two radicals, CH₃ and SiCl₃. In fast reactions following this initiation step, CH₄, SiCl₄, and HCl are formed as the primary stable gasphase products. These results will allow MTS decomposition rates to be predicted with greater accuracy than was possible with earlier, global rate expressions.

The work sponsored by OIT is now being broadened to include boron nitride CVD, in conjunction with a major manufacturer of ceramic composites. Thin layers of boron nitride are of interest as "debond" coatings on fibers used in continuous fiber ceramic composites, making them more resistant to cracking under load. The group is also investigating, under ARPA sponsorship, high-temperature reactions leading to titanium diboride formation, with 3M Corporation, and the pyrolysis of hydrocarbons used in the densification of carbon-carbon composites, with Textron Specialty Materials. 🤌



Reaction mechanism for the decomposition of MTS. Bold arrows indicate major reaction pathways.

Molecular transport in turbulence investigated

Alan Kerstein, Pat McMurtry (Professor of Mechanical Engineering, University of Utah), and Suresh Menon (Professor of Aerospace Engineering, Georgia Tech), with the help of graduate students, have performed several interrelated analytical and computational studies of molecular transport processes in turbulent flows. The focus of these studies was prediction and interpretation of the observable effects of the different molecular diffusivities of various chemical species and of heat in turbulent reacting flows.

It is generally recognized that these 'differential-diffusion' effects, particularly the rapid diffusion of hydrogen relative to other species, have significant impact on flame chemistry in laboratory-scale turbulent combustion processes. These effects complicate efforts to employ reduced chemical-kinetic mechanisms in models of these processes. It is less clear whether these effects continue to play a significant role in the larger scale, more strongly turbulent flows in commercial combustors.

Previous analysis of this scale-up issue suggested that the magnitude of differential diffusion effects is proportional to Re⁻¹, where the Reynolds number Re is a measure of turbulence

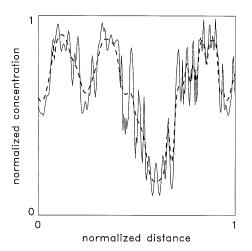
normalized concentration 0

normalized distance

intensity. The analysis was based on the well-established fact that species concentration fluctuations are generated at large scales and the fact that turbulent vortical motions cause these fluctuations to cascade down to small scales. Recognizing that differential diffusion is a fundamentally different process, in which fluctuations are generated at small scales and cascade up to large scales, Alan performed an alternative analysis that indicated a Re-1/4 dependence.

This slow falloff implies a previously unsuspected persistence of the complicating effects of differential diffusion in commercial-scale processes. To test the prediction, Alan and the Utah group performed numerical simulations of multispecies diffusion in turbulence using the linear-eddy turbulent mixing model that Alan developed previously for application to this type of problem. Illustrative results are shown in the plots. The Re^{-1/4} dependence was confirmed, and several other novel differential-diffusion effects were observed.

In a related study, Alan and the Georgia Tech group used the lineareddy model to simulate a hydrogenair turbulent jet diffusion flame using a full chemical-kinetic mechanism, including species-specific molecular



The linear-eddy model generates simulated one-dimensional profiles of instantaneous species concentration fields produced by turbulent mixing. Two typical pairs of profiles are shown, corresponding to low and high turbulence intensity (left and right, respectively). The Reynolds numbers for the two cases differ by a factor of ten. Solid and dashed profiles correspond to slow-diffusing and fast-diffusing species, respectively. In each simulation, the concentration fields of the slow and fast diffusers are initially identical. The differences between the profiles in each plot reflect the 'differential-diffusion' effect; profiles of the fast diffuser are smoother. The length scale of concentration fluctuations decreases markedly as turbulence intensity increases, but the magnitude of the concentration difference decreases more gradually, in accordance with predicted trends.

diffusivities. Comparison to results based on simplified chemical-kinetic schemes and/or simplified molecular transport (equal species diffusivities) indicated complicated interactions among flame chemistry, molecular transport, near-field heat release and far-field flow structure. A formulation with simplified transport and chemical kinetics was found to perform better than a formulation with simplified transport but full kinetics. This indicates a likely cancellation of errors in the simpler formulation; neither simplified formulation can be considered reliable over a wide range of operating conditions. It was concluded that predictions of NO production and related properties are sensitive to all the subprocesses considered.

All the results of these investigations point to the need for detailed chemistry and molecular transport submodels in computational models of turbulent combustion.



Stefan Steuerwald, a student of Professor Klaas Bergmann of the University of Kaiserslautern, visited the laboratory of David Chandler for several weeks last November to learn about the ion imaging technique. Stefan will utilize the technique in Germany to study bimolecular reactions.

Sandia National Laboratories, a prime contractor to the U.S. Department of Energy, is operated by Sandia Corporation, a wholly owned subsidiary of the Lockheed Martin Corporation.



Basic Energy Sciences peer review

The annual peer review of basic research supported at the CRF by the Department of Energy's Office of Basic Energy Sciences/Chemical Sciences Division occurred March 13-15. This year the review focused on research in combustion chemistry. Seated left to right are the reviewers, Prof. Richard Bersohn (Columbia University), Prof. Jürgen Wolfrum (Universität Heidelberg), Dr. Tim Wallington (Ford Motor Company), and Dr. Joe Michael (Argonne National Laboratory), along with Bill Kirchhoff (DOE). Standing are Allan Laufer and Tom York (DOE), Bill McLean, Larry Rahn, Frank Tully, and George Fisk.

Working meetings held with USCAR

The Engines Group, led by Jay Keller while Bob Carling was on special assignment at Ford Motor Company in Detroit, hosted members of the United States Council for Automotive Research (USCAR) on January 18 and 19. The group included John Hoard, Rick Anderson, and Dick Baker (Ford); Ron Herrin, Don Thorson, and Dave Harrington (GM); Tom Asmus (Chrysler); along with Pat Sutton (DOE), Charlie Westbrook, Bill Pitz, and Nick Marinov (LLNL), and Tye Barber (ORNL). The working group meeting was part of the Cooperative Research and Development Agreements (CRADAs) with the Low Emissions Partnership (LEP).

Sessions were held almost entirely in the laboratories of the principal investigators, e.g., Bob Green, Pete Witze, and Paul Miles, resulting in hands-on discussions. The industrial partners provided constructive guidance that will optimize the effectiveness of Sandia's work.

The Engines Group now has four projects with U.S. automobile manufacturers. Two CRADAs, signed at the end of January, are funded by the Defense Programs Technology Transfer Initiative. The other two projects are funded by DOE's Office of Transportation Technologies and have been in place for about a year.



Peter Hinze (right), working with Professor Wai Cheng of MIT, visited with Paul Miles (center) and Pete Witze (left) to obtain laser-Doppler-velocimetry turbulence measurements in a Sandia research engine. Peter and Wai are studying flame quenching due to strain for different levels of exhaust gas recirculation at idle conditions. Their research is funded by a consortium that includes the Big Three automakers.



(From left) Assaad Masri and Bassam Dally of Sydney University visited the Turbulent Diffusion Flame laboratory to work with Greg Fiechtner, Rob Barlow, and Tom Prast on multi-scalar measurements of bluff-body stabilized flames of methanol, $H_{\rm 2}/CO$, and $H_{\rm 2}/CH_{\rm 4}$ fuels. Velocity measurements in the same flames will be completed in Sydney, and the combined data will be compared with results from turbulent combustion models.

Pia Magnussen (right), University of Trondheim, Norway, was a visiting researcher last summer, working with Habib Najm (left) and Bob Schefer (center). She worked with Habib on the development of a fast Fourier transform Poisson solver for implementation into a numerical model for turbulent reacting flows and with Bob on the application of laser diagnostics to combusting flows.



Team develops a pulse-combustor design code

Pamela Barr and Jay Keller are developing a user-friendly PC-executable computer code to assist engineers both in designing pulse combustors for specific applications and in refining existing units. This code, named the Sandia Pulse Combustor Design Code, or SPCDC, represents the culmination of over ten years of research and development in the field of pulse combustion that has been funded by the DOE, GRI, and others.

The advantages of pulse combustors are numerous. Heat-transfer rates enhanced by the large oscillations in the flow field have been measured at up to 2.5 times greater than those obtained for steady turbulent flows at the same mean Reynolds numbers. This means that a smaller furnace can be used to provide the same energy output.

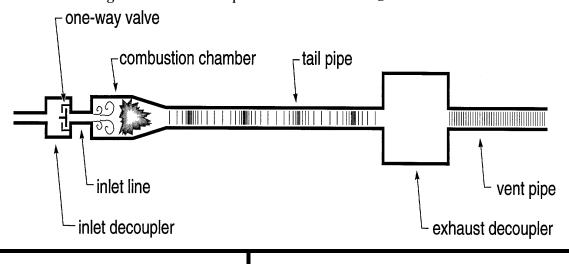
Also, pulse combustors do not require expensive auxiliary equipment such as external blowers or flues. The pressure oscillations draw in the supply of fuel and air, and the resulting thrust vents the exhaust products through a small diameter plastic pipe. This allows more flexibility in siting the unit and results in low maintenance expenses because there are few moving parts.

Another advantage of gas-fired pulse combustors is the low NO_X level in the exhaust gas, as low as 3 ppm, obtained without additional pollution control equipment. The main disadvantages are noise and vibration, but the physical structure can be designed to reduce these problems.

In order for there to be repeatable combustion-driven oscillations in a pulse combustor, the periodic combustion process and the resonant pressure wave must be in phase so that Rayleigh's criterion is satisfied. Previous experimental and computational studies at Sandia have shown that in premixed systems, fluid dynamic strain is responsible for suppression of reaction during injection, thereby ensuring that combustion occurs after the low-pressure portion of the cycle. This insight gained from the DOE-funded research is being incorporated in the development of the computational pulse combustor design tool supported by GRI, under the management of Jim Kezerle.

SPCDC is evolving from a research tool into a user-friendly engineering tool. It was originally developed to help understand the coupling among the acoustics, the injection, and the energy release for a research combustor configuration. Many algorithms have been added to the research code to make SPCDC useful to pulse-combustor manufacturers. The model's predictions have been compared against data from commercial and prototype hardware. Engineers representing U.S. companies that manufacture pulse-combustion systems are helping to guide the development of SPCDC.

This tool will be used by industrial engineers to optimize a design for specific applications, or to scale up a design to a desired input power rate. SPCDC should be available for general distribution toward the end of 1995.



Schematic of a Helmholtz-type pulse combustor showing the geometry of the primary components, which are modeled in the Sandia Pulse Combustor Design Code.



Published bimonthly.

For more information please contact:

William J. McLean Combustion Research Facility Sandia National Laboratories P.O. Box 969 Livermore, California 94551-0969 (510) 294-2687 ADDRESS CORRECTION REQUESTED

BULK RATE U.S. POSTAGE PAID LIVERMORE, CA 94551-0969 PERMIT NO. 234